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Thermal instabilities in the normal state of cuprate superconductors

R.A. Vargas and M. Chacón
Departamento de Física, Universidad del Valle
Apartado aéreo 25360, Cali, Colombia

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Abstract. High-resolution thermal analysis was performed on the high-T_c superconductors $LnBa_2Cu_3O_{7-x}$ (Ln = Nd, Sm, Ho, Er) between 80 and 300 K by an ac-calorimetry method. Apart from the usual "jump-like" anomaly in the heat capacity (C_P) at the superconducting transition temperature, T_c, a reproducible thermal anomaly in the ac-data from all superconducting samples in the 200-250 K temperature range also was observed. Since similar observations were made for Y- and Bi-based cuprates, these results show evidence of a common phase change in the normal state of the cuprate superconductors.

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1. Introduction

It is well known that the dominant structural feature of the cuprate superconductors is the layered structure with metallic Cu-O planes separated by thick semiconductive or blocking layers, which gives rise to a pronounced material anisotropy for current carrying and other transport processes [1-4]. Moreover, since the CuO_2 planes are universally present in the high-T_c cuprates, it is generally believed that this planes are responsible for the higher T_c found in these materials.

Many general trends of the superconducting properties of the copper oxides have emerged from numerous studies to elucidate the superconducting mechanism of these high-T_c materials; such as the dependence of T_c on carrier concentration —in particular, how the underlying electronic structure evolves as the insulating parent compounds are doped with electrons or holes to render them metallic and superconducting [2]. However, more work is required to separate sample-dependent effects from the observed properties in the superconducting as well as in the normal states of these cuprate superconductors.

Several studies [6–16] have focused on phase transitions and their possible relation to superconducting properties in the copper oxides. Raman scattering [9] and elastic studies [10], for instance, indicate at least a phase transition in $YBa_2Cu_3O_{7-x}$ (hereafter referred to as Y-123) in the 200-250 K temperature range. A peak that appeared below 240 K in the Raman spectrum of Y-123 was attributed by the authors [9] to oxygen ordering along an alternate sublattice; such ordering changes the hole concentration at the Fermi surface. Recently, measurements of longitudinal and shear velocities in $(Bi_{0.9}Pb_{0.1})_2Sr_2Ca_2Cu_3O_{10+x}$ (hereafter referred to as Bi-2223) have shown hysteretic behavior of both velocities between 100 and 250 K; the authors attributed the anomaly at 250 K to a distortion in the CuO_2 planes. Laegreid *et al.* measured specific heat in Y-123 during warming and found anomalies near 90 K and near 220 K; they interpreted the latter anomaly as arising from oxygen-atom ordering [16].

In previous papers [13,14], we studied the thermal properties of Y-123 and Bi-2223; similar thermal instabilities were found for both oxides in the 200–250 K temperature range. This paper presents the results of an ac-calorimetry study performed on other well-characterized single-phase polycrystalline samples of the 123 oxides above T_c with the prime objective of determining to what extent the previous observation is a result of the cuprates.

2. Experimental procedures

Samples with the nominal composition $LnBa_2Cu_3O_{7-x}$ (Ln = Nd, Sm, Ho, Er) were prepared from high purity powders of Ln_2O_3, $BaCO_3$ and CuO (99.9% purity) by the same solid state reaction method described in Ref. [17]. The procedures of calcinating, presintering and sintering were performed in an oxygen flow. The crystalline phase of these samples was characterized at room temperature by powder X-ray diffraction with CuK_α radiation. A detailed examination of the X-ray patterns revealed no crystalline impurity traces greater than 5% per volume, so a predominantly single phase ceramic with an orthorrombic unit cell was prepared for all samples. The X-ray characterization was made for each sample with reference to now available standards of several secondary phases and the orthorrombic phase for the 123 compounds. For example, the main reflections from a Nd-123 sample could be completely indexed with lattice parameters of $a = 3.89$ Å, $b = 3.87$ Å and $c = 11.67$ Å. The samples were further characterized by resistivity measurements, which were performed by the conventional dc four-probe method.

The heat capacity measurements were performed using an ac-calorimeter, described previously [18]. The samples, typically of several square millimeters in area and about 0.15 mm thickness, were hung from the thermal bath by two pairs of flattened chromel-alumel thermocouple wires, 25 μm diameter, attached on the rear face with a negligible amount of silicon grease. The front face of the sample was exposed to chopped light heating from a halogen lamp, through quartz windows in the cryostat. The amplitude of the induced temperature oscillation, $|T_{ac}|$, at frequency $\omega/2\pi = 2$ Hz of the heating pulses was detected with a lock-in amplifier, from which the relative heat capacity of the sample can be obtained with a precision to 0.1%, according to the basic equation of the ac-calorimetric method, $C_P = K/|T_{ac}|$. The calibration constant, K, was not obtained, so the reported C_P data correspond to $1/|T_{ac}|$ on a scale of arbitrary units.

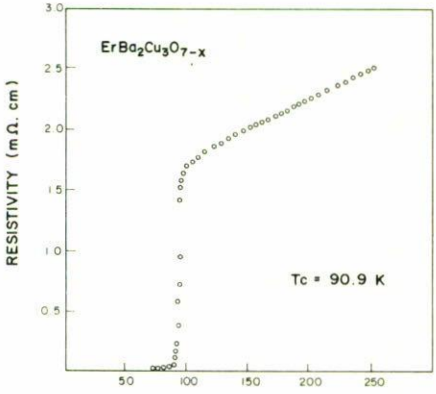

FIGURE 1. Resistivity of $ErBa_2Cu_3O_{7-x}$ as a function of temperature.

3. Results and discussion

Only samples with sharp resistive transition were used for the heat capacity measurements. A typical resistance against temperature curve for an Er-123 sample is shown in Fig. 1, in which the "zero resistance" was achieved at 90.9 K.

The heat capacity was measured on a portion of the same sample that was used for the resistivity analysis. Fig. 2 shows a typical $C_P(T)$ plot near 91 K for a Nd-123 sample. In this region, the ac-trace on a thermal cycling (during cooling an heating runs) shows the usual "jump-like" anomaly near T_c, which is in accord with the transition temperature observed in the resistivity measurements. Above T_c, the heat capacity is essentially normal for all samples, but a marked anomaly is shown near 220 K. On cooling runs from above 250 K, the ac-curves become different from those obtained in the warming stages down to approximately 200 K. On an amplified scale, Fig. 3 shows this region for $LnBa_2Cu_3O_{7-x}$ (Ln = Sm, Ho, Nd) samples; all of them display hysteretic behavior. The hysteresis loop for each sample is retraced on subsequent thermal cycles and it is independent of the thermal history of the sample and the rate of temperature cycling.

Previous measurements [19] of heat capacity in pure CuO ceramic have shown two easily observable peaks at 228.3 K and 211.6 K, respectively, which were associated with two consecutive magnetic phase transitions of this oxide in the 200–250 K temperature range. We have also confirmed that small amounts of CuO as a second phase in the cuprate superconductors produce two distinct anomalies in $C_P(T)$ at the same temperatures as those for pure CuO, and no hysteresis is detected between successive heating and cooling runs. Therefore, this result clearly indicates that the anomalous behavior of the heat capacity in the normal-state of the cuprate superconductors is not connected with the presence of CuO impurities in the samples. However, due to the common structural feature of the high-T_c cuprates of forming layered arrangements of the Cu and O ions, it seems natural to imagine

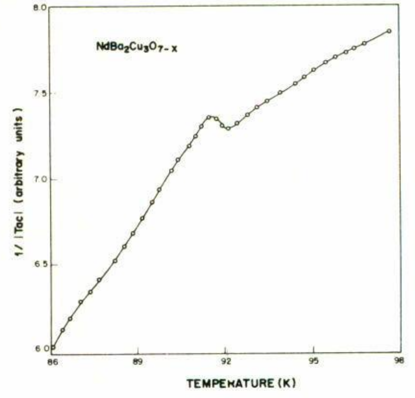

FIGURE 2. ac-calorimetric heating curve, $1/|T_{ac}|$, which is proportional to the heat capacity C_P, versus temperature for a $NdBa_2Cu_3O_{7-x}$ sample, in the vicinity of the superconducting transition.

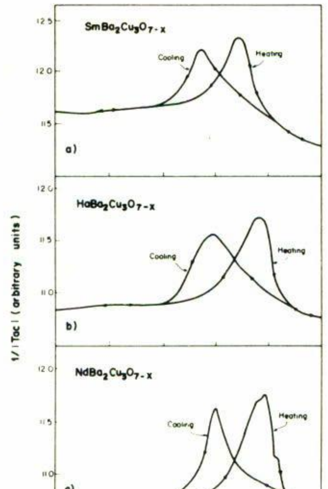

FIGURE 3. Heating and cooling $1/|T_{ac}|$ traces, which are proportional to the heat capacity C_P for: a) $SmBa_2Cu_3O_{7-x}$; b) $HoBa_2Cu_3O_{7-x}$; c) $NdBa_2Cu_3O_{7-x}$ samples, in the 135–260 K temperature range.

that the common thermal anomaly observed in all cuprate superconducting samples is entirely due to structural instabilities in their Cu-O layers.

It should be pointed out that the resolvable thermal anomaly in the 200–250 K temperature region of all tested superconducting cuprates seems to be insensitive to T_c and to the width of the superconducting transition region, so this anomalous behavior cannot be connected with the carrier concentration and its mobility, but with the ionic processes in the Cu-O subsystem.

In summary, our heat capacity measurements show thermal hysteresis that indicates strong evidence of a phase transition in Ln-123 (Ln = Nd, Sm, Ho) superconductors in the 200–250 K region, as has been previously suggested from quite different observations [6–9]. Since results similar to those reported here hold for the Y-123 and Bi-2223 compounds [10–16], then the common $C_P(T)$ anomaly in the same temperature range above T_c of the cuprates suggests the existence of common unstable phonon branches in the Cu-O planes that drive the phase transition.

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Resumen. Se realizó un análisis térmico de alta resolución en los superconductores de alta temperatura crítica $LnBa_2Cu_3O_{7-x}$ (Ln = Nd, Sm, Ho, Er) entre 80 y 300 K por un método de calorimetría ac. Aparte de la anomalía usual en forma de salto de la capacidad calorífica (C_P) en la temperatura de transición superconductora, T_c, se observa también una anomalía térmica reproducible en los datos ac de todas las muestras superconductoras en el rango de temperatura 200-250 K. Puesto que se tiene una observación similar para los cupratos basados en Y y Bi, estos resultados evidencian un cambio común de fase en el estado normal de los cupratos superconductores.